https://dx.doi.org/10.22161/ijaers.4.2.26 *ISSN: 2349-6495(P) | 2456-1908(O)*

Energetic Diffusion in ternary sets of Ge-Se-In Chalcogenide Glasses

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***Abstract*—** *The composition dependence of energetic parameter (A) in two sets of Ge-Se-In glasses, namely, Ge10Se90-xInx (x = 5, 10, 15, 20) and $Ge_{15}Se_{85-x}In_x$ (x = 0, 5, 10, 15, 20) have been studied by using rigidity percolation theory and bond constraints theory. Parameter (A) shows a local maxima at <r> = 2.67. The results are discussed on the basis of the topological and rigidity theory exhibited by covalent network glasses. The relative sensitivity of parameter (A) to these phenomena discussed.*

***Keywords*:-Chalcogenide glasses, Energetic parameter.**

I. INTRODUCTION

Chalcogenide glasses containing metal atoms form an interesting class of amorphous semiconductor (ASC) because of their potential applications as switching and memory devices. The additions of metals to these glasses increase the average coordination number and, thus, transform the network from one with a soft structure to one which is nearly tetrahedral. Glasses containing Se are known to consist of a mixture of long chains and Se8 rings [1]. The addition of Ge with Se forms very good covalently bonded glass. The dominant feature of the network is fourfold coordinated Ge [2]. Ge-Se glasses have been particularly studied because of their ready glass formation, easy synthesis requirements and good chemical stability [3]. Experimental results reported by various researchers have shown that the addition of impurity atoms in binary Se-Ge and Se-In systems does change the physical properties like optical, electrical and thermal, of chalcogenide glasses significantly [4– 6]. It has also been found that the effect of impurities depends strongly on the composition of the glass, the chemical nature of the impurity and the method of doping. Impurity concentration is obviously a critical factor in such cases because all impurities cannot behave in an electrically active manner. Several of the physical properties are found to improve by the addition of certain impurities. Therefore, investigations on the influence of impurities on the properties of chalcogenide glasses are of relevance both from the basic science and application point of view.

Among all chalcogens, Se is one of the most important chalcogen element, as it has applications in electrograph. The pure Se has disadvantage due to its short life time and low sensitivity, which can be improved by incorporation of group III, IV, V, and VI elements like Ga, In, Ge, As, Sb, Bi, Te, etc. The work on binary Se alloys has already been reported [7–9]. Se-Ge has been used as a base material and incorporation of In as the third element has been studied [10-11]. The addition of the third element expands the glass forming area, and also, creates compositional and configurationally disorder in the system. Generally, the binary alloys are covalent in the nature and the addition of third element creates iono-covalent bonds and as a result the conduction increases.

In the present work we have reported the theoretical prediction of the compositional effect on the spectral dependence of the absorption or energetic diffusion in $Ge_{10}Se_{90-x}In_x$ (x = 5, 10, 15, 20) and $Ge_{15}Se_{85-x}In_x$ (x = 0, 5, 10, 15, 20) glassy system .An attempt has been made to explain the varying trends of various parameters with increasing In content.

II. RESULT AND DISCUSSION

The Ge-Se-In ternary system is a prototypical chalcogenide glassy system and form bulk glasses over a wide range of composition expected up to 25% at %In and up to 60-90% at % Se with reminder being Ge [12]. Models based on chemical ordering [13] and network topology [14-17] has been proposed to explain the composition dependence of physical properties. The chemically ordered network (CON) model favors the formation of heteropolar bonds and thus the glass structure is composed of cross linked structure units of stable chemical compounds and excess, if any, of the elements. It has been argued that chemical ordering leads to a chemical threshold at which specific features in the composition dependent variations occur [18]. The

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topological model is based on balancing the number of operative constrains with the number of degree of freedom. This model describes the composition dependence in terms of the average coordination number <r> and predicts a topological threshold at <r> = 2.4, where the rigidity of the network percolates [19]. The network is floppy below <r>=2.4 and rigid above <r> = 2.4. A later modification of this model [20] based on the formation of two dimensional layer structures and medium range interactions suggests a topological threshold at <r>= 2.67 where a change from two dimensional layered structure to three dimensional network takes place due to cross-linking.

The applicability of the ideas of rigidity percolation was verified in many binary and ternary glasses [21-22]. Signature of rigidity percolation has been reported to occur at 2.4 or near 2.67 in various glasses. In this paper , we present results on the composition dependence of optical energy gap in three sets of Ge-Se-In glasses , namely $Ge_{10}Se_{90-x}In_x$ (x = 5, 10, 15, 20) and $Ge_{15}Se_{85-x}In_x$ (x = 0, 5, 10, 15, 20). The composition range covers the threshold composition predicted on the basis of various models .In terms of average coordination number <r>, calculated using the formula-

$$\mathbf{<r> = [(X)ZGe + (Y)ZIn + (100-X-Y)ZSe] / 100}$$

Where Z_{Ge} = 4, Z_{In} = 4 and Z_{Se} = 2 are the coordination number of Ge, In and Se respectively the compositions fall in the range 2.20 < (r) <2.70.

The spectral dependence of the absorption coefficient indicates an indirect allowed transition. The result is verified by energetic parameter relation Vs. composition. According to Angell proposal [23], the compositional changes in the optical gap is correlated by energetic parameter (A) which is given by the equation-

$$\mathbf{A = \underline{\epsilon \Delta Eg} / k}$$

Where Є = δ (z-2) and k = Boltzmann constant (1.38 x 10-23 J/Kelvin), δ is an independent constant (0.55).

The variation of energetic parameter (A) as function of average coordination number <r> for the two sets of glasses studied is given in Fig.- 1. It can be inferred that the two sets of glasses show identical trends in the <r> dependence. Energetic parameter (A) increases initially <r> is increased and then exhibit a local maximum at <r> = 2.67. An explanation of the observed behavior can be given in the framework of the energy band model for the

Chalcogenide glasses proposed by Kastner [24] and the change in the average bond energy of the system as the composition varied. According to the Kastner the valance band in the chalcogenide glasses is constituted by the lone-pair bands where the conduction band arises from the anti-bonding band. In a multi-component glass like Ge-Se-In the position of conduction and valance band edges and thus the energy gap largely depends on the relative number of various possible bonds in the system and the average bond energy. The various possible bonds in the Ge-Se-In system are Ge-Se, Se-Se, Se-In, Ge-Ge, Ge-In and In-In. The bond energies are 231.11, 189.22, 257.5, 185, 146.06, and 217kJ/mol respectively. The values of average coordination number<r>, energy gap (Eg) and energetic parameter (A) for the two glassy systems are listed in table:-1 and table: -2

The observed initial increase in Eg with increase in <r> suggests that in this region of curve the influence of the relative number of Se-Se and In-In bond are less prominent in determining the band gap than that of the GeSe2 structural unit. It appears that Ge-Ge bonds are present in all these compositions. The increase in Eg continuous under the influence of the relative decrease in the number of strong Ge-Ge bonds. The composition with <r>> 2.67 contains a large concentration of relatively strong In-In bonds resulting in a increase in Eg. However, it may be mentioned that <r> = 2.67 also corresponds to the topological threshold suggested by Tanaka [11] based on the formation of a layered structure and medium range interactions.

III. FIGURE AND TABLES

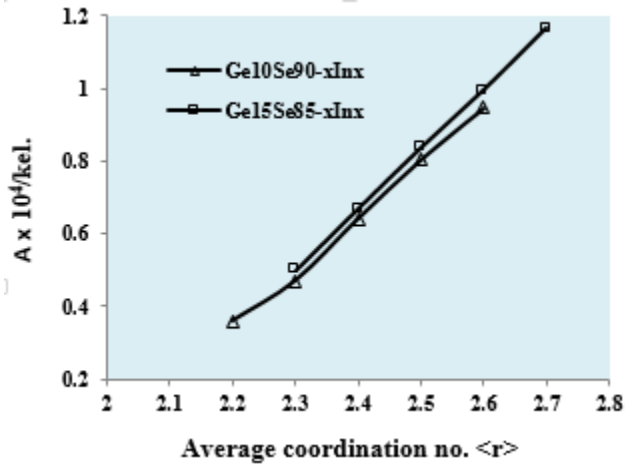

Fig.1: Variation of Energetic parameter (A) with average Coordination Number <R> for the two sets of Ge-Se-In Glasses

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Table.1: Value of <r>, E_g and A for $Ge_{10}Se_{90-x}In_x$

X%	<r>	E_g(eV)	A x 10^4/kel.
0	2.20	2.497	0.3584
5	2.30	2.506	0.4694
10	2.40	2.514	0.6412
15	2.50	2.521	0.8038
20	2.60	2.529	0.9576

Table.2: Value of <r>, E_g and A for $Ge_{15}Se_{85-x}In_x$

X%	<r>	E_g(eV)	A x 10^4/kel.
0	2.30	2.576	0.4928
5	2.40	2.583	0.6688
10	2.50	2.590	0.8358
15	2.60	2.598	0.9941
20	2.70	2.607	1.1637

IV. CONCLUSION

The variation of energetic parameter (A) of the two sets of Ge-Se-In glasses studies show features at different <r> values. These results can be interpreted as a signature of two different phenomena occurring in this system, namely, the chemical threshold and the topological threshold. Since Eg is more sensitive to variations of the relative number of different bonds and the average bond energy of the system. The local maximum in the Eg and parameter A variation is the signature of the chemical ordering occurring in the system at <r> = 2.67. Hence both chemical and topological threshold exhibit in the Ge-Se-In system and manifest in the properties that are sensitive to either of the phenomena.

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